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PARTICULARS OF HYDROTHERMAL SYNTHESIS OF NANOSIZE POWDER $(Zr_{1-x}Y_x)O_y$

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Nanocrystalline $(Zr_{1-x}Y_x)O_y$ powders were synthesized by a method combining co-precipitation and hydrothermal decomposition. The granulometric composition was certified, x-ray phase analysis was performed, and the pycnometric density of the synthesized powder was determined.

Key words: hydrothermal synthesis, stabilized zirconium dioxide, nanocrystalline powders.

The unique combination of properties of stabilized zirconium dioxide — high mechanical strength, fracture toughness, refractoriness, chemical resistance and bioinertness — make it an irreplaceable material in a number of modern technological processes and practices, ranging from metallurgy and machine engineering to stomatology.

It has been determined that most properties of solids become size-dependent as particle size decreases to several interatomic distances in one, two or three dimensions. A strong nanostructural ceramic based on ZrO_2 with a significant increase of mechanical properties can be obtained on the way to developing a material with a fine uniform structure [1]. Therefore, nanocrystalline ceramic powders with prescribed morphology, phase composition and properties of the bulk phase and surface are required for the production of different ceramic materials and devices of a new generation, such as sensors, storage batteries, high-density ceramic articles and effective heterogeneous catalysts and sorbents.

An entire series of methods is used to obtain nanocrystalline zirconium dioxide [2 – 9]. The use of different methods of synthesis results in the formation of ZrO_2 nanocrystals with different crystal structure and morphology with different and, as a rule, quite wide particle-size distribution. In addition, the technological parameters of the formation of nanocrystalline zirconium dioxide vary significantly not only from one method to another but also with a single method [4 – 6, 10]. Hydrothermal synthesis is widely used because it offers the possibility of obtaining practically isolated ZrO_2 nanocrystals with a quite narrow particle-size distribution. In spite of the diversity of the published works on the synthesis of ZrO_2 nanocrystals under hydrothermal conditions there is no concensus of opinion concerning the temperature and mechanism of formation of zirconium dioxide nanocrystals under hydrothermal conditions. The production by the hydrothermal method of nanocrystalline powders of metal oxides from water solutions of salts involves technological difficulties and requires significant temperatures, very high pressure and special equipment. For this reason it is necessary to use a combined method [11], which consists of obtaining beforehand a precipitated mixture of hydroxides followed by their high-temperature hydrothermal decomposition.

The co-precipitation method makes it possible to attain at the molecular level a high degree of homogeneity of the initial mixtures, while high-temperature hydrolysis promotes the formation of weakly agglomerated primary nanocrystalline ZrO_2 particles.

EXPERIMENTAL MATERIALS AND PROCEDURE

The chemical precipitation of zirconium and yttrium hydroxides was conducted in a 1 M solution of zirconyl nitrate and yttrium acetate in distilled water with 0.01 wt.% oxyethylated nonylphenol solution of ammonia.

The precipitate obtained was washed to remove the nitrates formed. The nitrate concentration after washing should not exceed 10 mg/liter. The milk-colored suspension obtained was centrifuged with rate 2000 rpm to increase the percentage volumetric content of matter. The gel obtained was loaded into a 5-liter R-401 supercritical reactor (South Korea), where hydrothermal decomposition occurred.

The internal pressure of the reactor was controlled by varying the temperature of the heater and by the water-cool-

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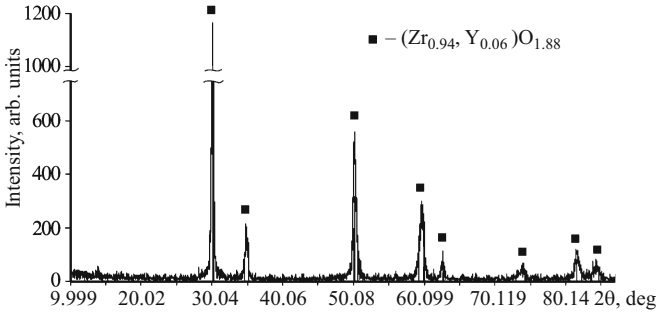
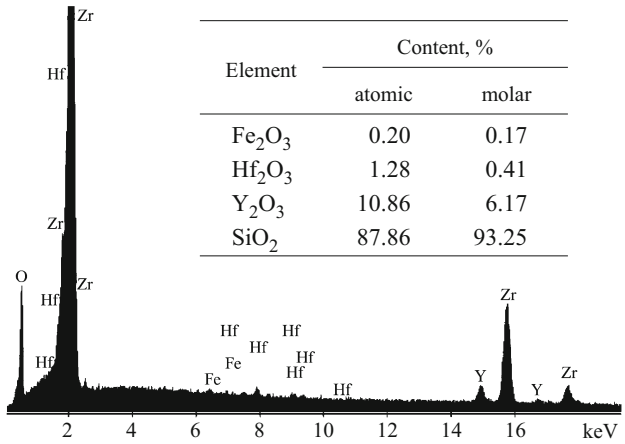


Fig. 1. X-ray diffraction pattern of the synthesized powder $(Zr_{0.94}Y_{0.06})O_{1.88}$ after hydrothermal decomposition of co-precipitated yttrium and zirconium hydroxides.



Element	Content, %	
	atomic	molar
Fe_2O_3	0.20	0.17
Hf_2O_3	1.28	0.41
Y_2O_3	10.86	6.17
SiO_2	87.86	93.25

Fig. 2. EDAX analysis of $(Zr_{0.94}Y_{0.06})O_{1.88}$ powder after hydrothermal decomposition of co-precipitated yttrium and zirconium hydroxides.

ing system of the reactor chamber. The powder obtained was dried in a drier at temperature 80°C for 2 h and then heated in a muffle furnace at temperature 300°C in air for 1 h in order to remove residual water.

Specifically, 35.27 g of zirconyl nitrate $(ZrO_2(NO_3)_2)$ and 1.41 g yttrium acetate $(YC_6H_9O_6)$ were used to obtain 20 g of zirconium dioxide powder stabilized by 6% yttrium.

The phase composition of the synthesized yttrium-stabilized zirconium dioxide powder after heating was determined by x-ray phase analysis (Rigaki Ultima IV, CuKα radiation, Ni filter).

The precise elemental composition of the material was determined by x-ray phase analysis performed with a Quanta 200 3D scanning ion-electron microscope.

A JEM-2100 transmission electron microscope was used to determined the shape and size of the particles of $(Zr_{1-x}Y_x)O_y$ powder.

An AccuPyc II 1340 helium pycnometer was used to determine the density of the synthesized powder.

EXPERIMENTAL RESULTS AND DISCUSSION

It was determined that the process of hydrothermal decomposition of zirconium dioxides occurs in a wide range of temperatures and pressures, starting with the subcritical state of water vapor 180°C — 50 bar up to the supercritical state where the temperature and pressure in the reactor reach 400°C — 250 bar. The reaction time is 45 min when the working parameters are reached.

In the model experiment on obtaining zirconium dioxide stabilized by 6% yttrium it was determined that according to the ICDD card index data the material obtained is the single-phase solid solution $(Zr_{0.94}Y_{0.06})O_{1.88}$ (Fig. 1) and possesses a tetragonal crystalline lattice with space group P42/nmc and the lattice parameters $a = 3.6020$ Å, $b = 3.6020$ Å, $c = 5.1790$ Å, $\alpha = 90°$, $\beta = 90°$ and $\gamma = 90°$.

To determine the precise elemental composition of the material x-ray spectral analysis was performed using a Qunata 200 3D scanning ion-electron microscope. It was determined that the composition of the synthesized material corresponds to the required composition $(Zr_{0.94}Y_{0.06})O_{1.88}$ (Fig. 2).

The investigation of $(Zr_{0.94}Y_{0.06})O_{1.88}$ powder performed with a transmission electron microscope (TEM, JEM-2100 microscope) showed that the powder consists of spherical particles of average size 3 – 15 nm (Fig. 3), and the weakly bound agglomerates are no bigger than 500 nm.

The helium pycnometry investigation of the density of the powders obtained showed that on average the density of the powders obtained is higher than 90% of the theoretical density of zirconium dioxide. This result indicates the presence of absorbed water on the surface of the nanoparticles. It should be underscored that all experimental samples were obtained by drying from suspensions. This gives powders with a characteristic porous structure comprised of primary nanodisperse particles united into conglomerates. The porosity in such systems consists of two components: gaps between primary particles, which determine the capability of the powder to absorb water from the ambient atmosphere, and closed pores in which water remains even after the samples are dried to a constant mass.

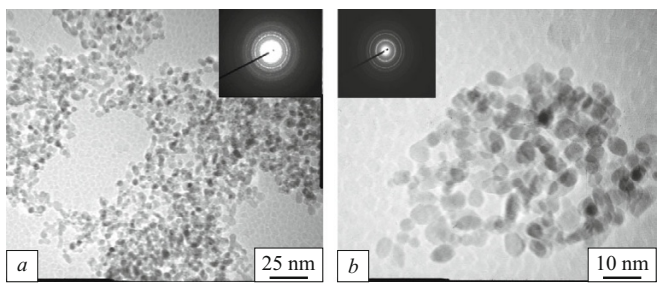


Fig. 3. TEM image of synthesized nanoparticles of $(Zr_{0.94}Y_{0.06})O_{1.88}$ powder: *a*) 350°C, 250 bar; *b*) 215°C, 100 bar.

CONCLUSIONS

The following technical result was obtained by using the present synthesis method:

– nanosize zirconium dioxide powder stabilized by yttrium oxide $(Zr_{1-x}Y_x)O_y$ in the tetragonal modification;

– crystallite sizes 3 – 15 nm;

– size of weakly bound agglomerates 100 – 500 nm;

– yield of the final product ≥ 85% of the theoretical value.

The approach developed here makes it possible to obtain high-purity weakly agglomerated nanosize powder of stabilized zirconium dioxide for fabricating ceramic articles directly from zirconium dioxide and composite materials based on it, which are used in machine engineering, the chemical and power-generation industries and medicine.

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